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2-Polyfluoroacylcycloalkanones in Reactions with Selected Phosphorus(III) Compounds

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ABSTRACT: *The reactivity of 2-polyfluoroacylcycloalkanones and their O-silylated derivatives towards phosphites and tris(trimethylsilyl)aminoiminophosphine has been investigated. From α-polyfluoroalkyl substituted phosphonates, generated from tris(trimethylsilyl) phosphite and 1,3-diketones, the respective phosphonic acids and their salts have been obtained. In one case, upon warming, a phosphonic acid underwent a ring closure to yield an oxaphospholene. 2-Trifluoroacetylcycloalkanones and diethyl isocyanatophosphite furnished phosphoranes diastereospecifically, via addition of phosphorus at the trifluoroacetyl group and two additional heterocyclizations. Tris(trimethylsilyl)aminoiminophosphine formed very reactive trimethylsilylimino-1,2$\lambda^5\sigma^4$-phospholenes, which added hexafluoroacetone to give spirocyclic 1,3,2$\lambda^5\sigma^5$-oxazaphosphetanes. The structures of the new compounds were determined by NMR spectroscopy and X-ray single crystal analysis.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:97–107, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10001

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INTRODUCTION

Phosphorus(III) derivatives and 1,3-dicarbonyls are able to act as nucleophiles and electrophiles [1,2], respectively, thus permitting various reaction possibilities. The introduction of fluorine into the 1,3-dicarbonyls increases considerably their electrophilic reactivity as compared with the non-fluorinated analogues [3,4], thus giving polyfluorinated 1,3-dicarbonyls a special attraction. Furthermore, the unique lipophilic and electron withdrawing properties of the polyfluorinated substituents [5] in products from the reaction of the 1,3-dicarbonyls with phosphorus(III) compounds render them potentially applicable in medicinal and bioorganic chemistry. Here we report the investigations of the regio- and stereochemistry in the reactions of nonsymmetrical polyfluorinated 1,3-dicarbonyls, particularly those containing a cyclic fragment, with selected phosphorus(III) derivatives.

RESULTS AND DISCUSSION

The first step in the reactions of 1,3-dicarbonyls and their O-substituted derivatives with phosphites is considered to be a nucleophilic attack of phosphorus at the carbonyl carbon atom. The resulting adduct has two possibilities for further stabilization; either a ring closure to furnish a phosphorane ($\lambda^3\sigma^3$P $\rightarrow$ $\lambda^5\sigma^5$P, type **A**) [1,2,6–9] or a substituent migration

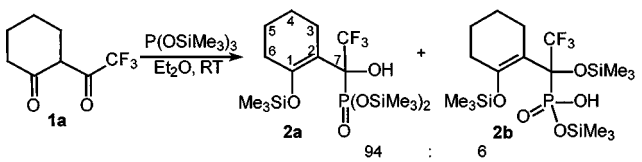
from the phosphite with formation of a phosphonate $\lambda^3\sigma^3P \rightarrow \lambda^5\sigma^4P$, type **B**) [1,2,10–12].

The reaction of 2-trifluoroacetylcyclohexanone (**1a**) with tris(trimethylsilyl) phosphite yields via nucleophilic attack of phosphorus at the trifluoroacetyl carbonyl carbon atom, followed by silatropy [10,13,14], a mixture of phosphonates **2a** and **2b** (94:6) according to type **B** (Scheme 1).

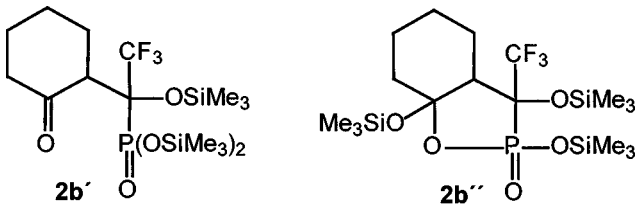
The δ_P values (−1.4 and 1.2) of coexisting compounds **2** are typical for phosphonates. In the $^{31}P\{^1H\}$ and ^{19}F NMR spectra of the predominant compound, the splitting of signals with $^3J_{P-F} = 5.1$ Hz confirms the relative positions of the CF_3 group and phosphorus. The δ_H(OH) value of 7.29 ppm is characteristic for a hydroxyl group in a geminal position with respect to a CF_3 group [15]. This and additional splitting with $^3J_{H-P} = 7.3$ Hz prompted us to assign the set of signals with the higher intensity structure **2a**. Molecule **2a** has a chiral centre, causing AB-systems for the protons of each CH_2 group, one of which is resolved, and nonequivalence of the trimethylsilyl substituents. In the ^{13}C NMR spectrum, only signals of **2a** can be observed. The δ_C values for C^1 and C^2 (151.0 and 109.5 ppm, $^3J_{C-P} = 9.8$ Hz) are due to the enolic C=C system. The signal at $\delta_C = 79.2$ ($^1J_{C-P} = 175.1$, $^2J_{C-P} = 28.6$ Hz) is assigned to the sp^3 CF_3C carbon nuclei indicating geminal arrangement of the phosphonate with respect to CF_3.

The small differences of the δ_F and δ_P values for **2a** and **2b**, present in much lower concentration, led us to propose that both compounds have a similar structure. The splitting of the signal with lower intensity in the ^{19}F NMR spectrum with $^3J_{F-P} = 5.2$ Hz (cf. **2a**: $^3J_{F-P} = 5.2$ Hz) confirms the geminal position of the CF_3 group with respect to phosphorus. The absence of a methyne proton signal in the ^1H NMR spectra prompted us to exclude structures **2b′** and **2b″** (Scheme 2).

To avoid trimethylsilyl migration to the HO function of 1,3-diketone, the enol O-silylated derivatives of 2-polyfluoracylcycloalkanones—compounds **3a** and **3b**—have been used directly, which, regardless of the state of the silatropy equilibrium [16], reacted with tris(trimethylsilyl) phosphite to give **4a** and **4b** as colourless, moisture sensitive, and viscous liquids in 73 and 75% yield, respectively (Scheme 3).



SCHEME 1



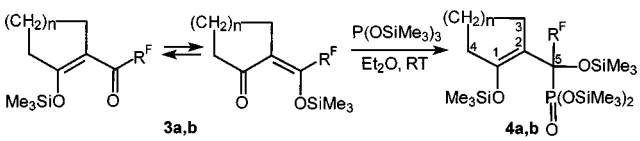
SCHEME 2

Obviously, this reaction is of type **B**: nucleophilic attack of phosphorus at the trifluoroacetyl moiety, followed by migration of one of the trimethylsilyl groups [10,13,14]. Phosphonate **4b** could be characterized only spectroscopically.

The δ_P values of **4a** (−2.2 ppm), and **4b** (−1.2 ppm) are characteristic of phosphonates. In the ^{19}F NMR spectra of both compounds couplings with $^3J_{P-F} = 8.6$ Hz are observed for the CF_3 and α-CF_2-signals (the same splitting is found also in the $^{31}P\{^1H\}$ NMR spectrum of compound **4a**), and this confirms the relative position of the CF_3 group and phosphorus. The structure was also confirmed by ^{13}C NMR data. The sp^3 character of the R^FC carbon nuclei is represented by δ_C = ca. 81. This signal shows an additional $^1J_{C-P}$ splitting, proving the attack of phosphorus at the polyfluoroacyl carbonyl group. Accordingly, the C^1 resonance shows a coupling with $^3J_{C-P} = 8.7$ (**4a**) and 8.2 Hz (**4b**), respectively. The chiral centre at C^5 induces non-equivalence of both of the Me_3Si moieties at the phosphonate fragment and the F-atoms of the CF_2 groups in **4b**, and for the C^5–CF_2 group an AB-system was found in the ^{19}F NMR spectrum.

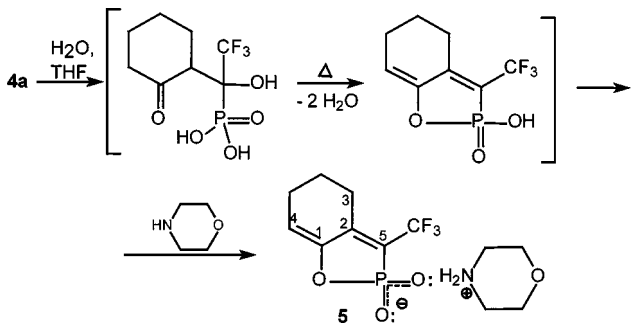
The hydrolysis of **4a** afforded the respective phosphonic acid, a viscous oil, which, upon warming, underwent a cyclodehydration to form an oxaphospholene, isolated as the morpholinium salt **5** (Scheme 4).

The NMR sprectroscopic data of **5** confirm the proposed structure, a triplet for the olefinic proton



3, 4	R^F	n
a	CF_3	2
b	C_3F_7	1

SCHEME 3

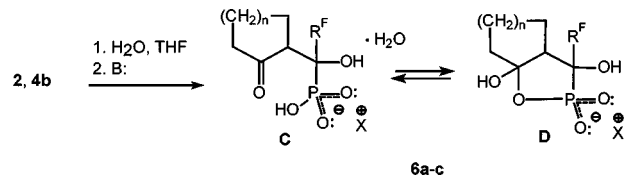


SCHEME 4

at C^4 in the ^1H NMR spectrum, no signal for a keto carbon nuclei and $\delta_C(C^1) = 147.0$ for the enol moiety in the ^{13}C NMR spectrum, and $\delta_C(C^4) = 147.0$ ($^3J_{C-P} = 9.7$ Hz) appears as a doublet in the "olefinic" region. The resonance of C^5 was observed at $\delta_C = 119.6$ indicating the sp^2 character.

The mixture of **2a, 2b**, and phosphonate **4b** has been hydrolyzed to give the respective phosphonic acids, isolated as potassium or morpholinium salts **6a–c** (Scheme 5).

In the solid state, compounds **6** are present in the monocyclic from **C**, confirmed by the single crystal X-ray structure determination of compound **6b** (Fig. 1; Tables 1, 2). The IR data of the solid **6a–c** gave additional evidence, since, in the 1695–1730 cm^{-1} region, C=O absorptions of a cycloalkanone were observed. NMR spectra measured in DMSO-d_6, however, exhibit two sets of signals. The relatively large difference in the δ_P values (up to 17 ppm) shows that the coexisting forms are not diastereomers of the general structure **C**. Comparing the δ_P values of similar compounds [12,17], one can assume a chain-ring tautomerism. The predominant compound is present as an open chain (form **C**, δ_P = 10–17), the less dominant isomer being bicyclic (form **D**, δ_P = 22–27).



Product	X	R^F	n	Starting Materials
6a	K	CF_3	2	**2a,b** and KOH
6b	K	C_3F_7	1	**4b** and KOH
6c	Morpholinium	C_3F_7	1	**4b** and morpholine

SCHEME 5

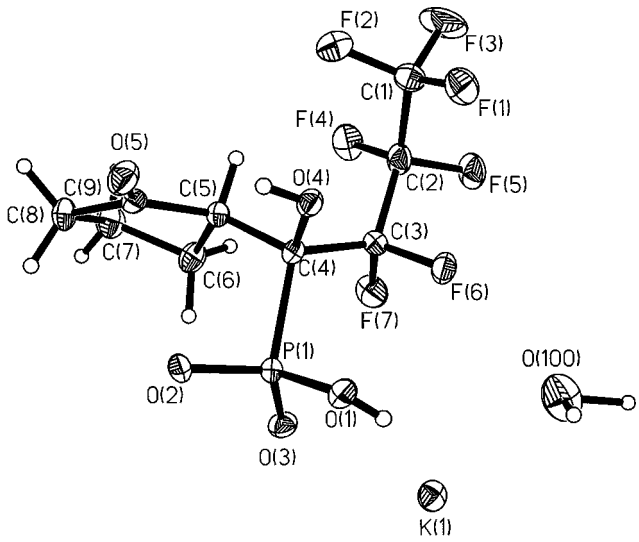


FIGURE 1 Molecular structure of compound **6b** (thermal ellipsoids with 50% probability).

Contrary to 1,1,1,5,5,5-hexafluoropentane-2,4-dione [1,6,8], the reactions of 2-trifluoroacetylcycloalkanones with trialkyl phosphites at room temperature and even upon warming in diethylether or THF furnish no products. Obviously, the stabilisation of the possible adduct according to type **A** or **B** is not possible. Refluxing of 2-trifluoroacetylcycloalkanones with trialkyl phosphites in toluene or benzene results in a complex mixture of nonseperable compounds.

The reaction of 2-trifluoroacetylcycloalkanones **1a,b** with diethyl isocyanatophosphite yields (type **A**) diastereospecifically the tricyclic system **7** irrespective of the ring size in the precursor compounds. Probably, product **F** is formed via intermediate **E** generated from the attack of phosphorus on the trifluoromethyl substituted keto carbon atom. Finally, the Z-hydroxy moiety adds across the P=N double bond (Scheme 6). Despite the presence of two chiral centres, only *one* diastereomer is obtained because of the limitation of the reaction channel numbers [9], proven from the NMR spectra, where only *one* set of signals has been observed.

Unlike its linear analog (ethyl 4,4,4-trifluorobutan-3-onate) [11], α-trifluoroacetyl-δ-valerolactone does not react with diethyl isocyanatophosphite. Surprisingly, only starting compounds are isolated from the reaction of pentane-2,4-dione with diethyl isocyanatophosphite.

The cyclopentane ring containing compound **7b** is moisture-sensitive, unlike the cyclohexane derivative **7a**. This may be due to the greater ring strain of the tricyclic cyclopentane phosphorane.

TABLE 1 Details of Crystal Data, Measurement of Intensities, and Data Processing of X-ray Investigation of Compounds **6b** and **9a**

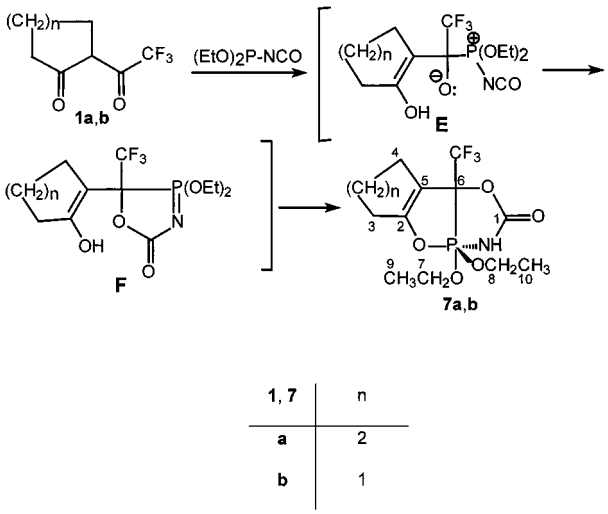
	6b[a]	***9a***[b]
Formula	$C_9H_{11}F_7KO_6P$	$C_{19}H_{34}F_8N_2O_3PSi_3$
FW	418.25	605.72
Crystal size (mm)	$0.8 \times 0.5 \times 0.2$	$0.8 \times 0.7 \times 0.6$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (pm)	623.0(2)	1151.4(2)
b (pm)	918.0(1)	2210.6(4)
c (pm)	2499.1(2)	1215.8(1)
α (deg)	90	90
β(deg)	96.26	104.99(1)
γ (deg)	90	90
V (nm^3)	1.4207(5)	2.9893(8)
Z	4	5
D_{calc} (Mg/m^3)	1.955	1.682
μ(Mo Kα) (mm^{-1})	0.599	0.356
2θ range (deg)	2.76–27.49	2.53–27.50
F(000)	840	1575
Index range	$-1 \le h \le 8$, $-1 \le k \le 11$, $-32 \le l \le 32$	$-1 \le h \le 14$, $-28 \le k \le 1$, $-15 \le l \le 15$
Reflections collected	4191	6760
Independent reflections	2800 [R(int) = 0.0426]	5285 [R(int) = 0.0288]
Completeness to θ_{max} (%)	86.0	76.9
Data/Restraints/Parameter	2800/0/237	5285/0/349
Goodness-of-fit on F^2	1.070	1.018
Final R indiced [$I > 2\sigma(I)$]	$R1 = 0.0515$, $wR2 = 0.1237$	$R1 = 0.0483$, $wR2 = 0.1179$
Largest difference peak and hole, (e.Å^{-3})	0.495 and −0.485	0.428 and −0.335
Weighting scheme ($P = (F_o^2 + 2F_c^2)/3$	$w^{-1} = \sigma^2(F_o)^2 + (0.0551P)^2 + 1.7399P$	$w^{-1} = \sigma^2(F_o)^2 + (0.0600P)^2 + 1.76P$

[a]Single crystals (colorless prisms) crystallized from *i*-PrOH:H_2O (2:1).
[b]Single crystals (colorless prisms) crystallized from hexane.

The NMR data confirm the proposed structures of **7**; the ^{31}P NMR shift values are typical for tricyclic phosphoranes [7,9,18], appearing at significantly lower field for the cyclopentane derivative **7b** ($\delta_P = -35.76$) than for cyclohexane derivative **7a** ($\delta_P = -49.03$). The shift value of C^6 (bonded to the CF_3 group) is found to be δ_C ca. 88, showing its sp^3 character. Additional $^1J_{C-P}$ splitting confirms the geminal position of CF_3 with respect to phosphorus. The $^1J_{C-P}$ values 124.1 (**7a**) and 129.6 Hz (**7b**)

TABLE 2 The Selected Bond Lengths (pm) and Angles (deg) of Compounds **6b** and **9a**

6b		***9a***	
K(1)—O(3)	286.9(3)	P(1)—N(2)	163.3(3)
P(1)—O(3)	149.4(3)	P(1)—N(1)	168.6(2)
P(1)—O(2)	151.0(3)	P(1)—O(1)	171.81(19)
P(1)—C(4)	189.7(4)	P(1)—O(3)	174.64(19)
C(3)—C(4)	153.7(5)	P(1)—C(6)	193.1(3)
C(4)—C(5)	154.5(5)	O(1)—C(5)	136.0(3)
C(4)—O(4)	142.7(5)	O(2)—C(6)	141.2(3)
C(9)—O(5)	121.2(5)	O(3)—C(14)	139.0(4)
O(3)—P(1)—O(2)	118.19(15)	N(1)—C(14)	144.8(4)
O(3)—P(1)—O(1)	112.54(16)	C(4)—C(5)	132.0(4)
O(2)—P(1)—O(1)	106.18(15)	C(4)—C(6)	148.8(4)
O(3)—P(1)—C(4)	113.33(16)	O(1)—P(1)—O(3)	168.75(10)
O(4)—C(4)—C(3)	103.3(3)	O(3)—P(1)—N(1)	76.94(10)
O(4)—C(4)—C(5)	110.4(3)	N(1)—P(1)—N(2)	124.68(13)
C(9)—C(8)—C(7)	105.3(3)	O(1)—P(1)—C(6)	92.26(10)
O(5)—C(9)—C(8)	125.5(4)	O(1)—P(1)—N(2)	92.93(11)
C(3)—C(4)—P(1)	111.3(2)	O(3)—P(1)—N(2)	93.22(11)



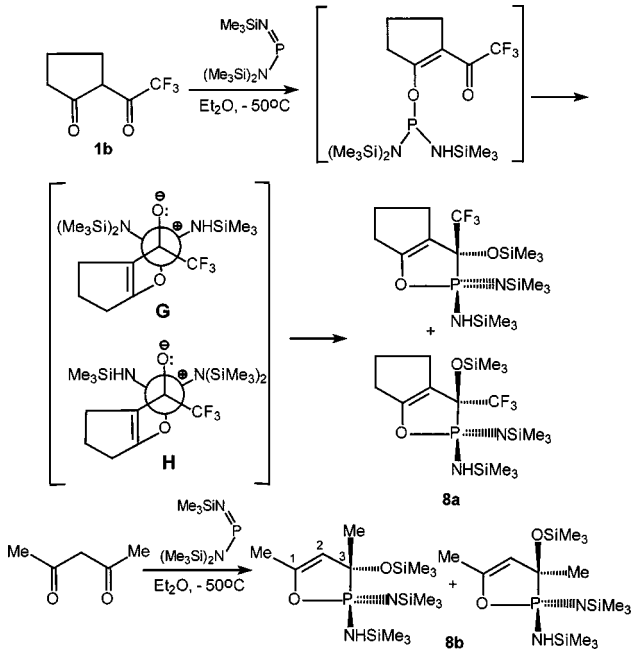
SCHEME 6

[7,18,19] indicate the equatorial-axial–equatorial arrangement of the two annellated five membered rings with carbon in an axial position. Pseudorotation is obviously not active, since axial and equatorial ethyl substituents could be distinguished, δ_H and δ_C values at lower field for the equatorial and at higher field for the axial position [9,17,20].

2-Trifluoroacetylcyclopentanone (**1b**) reacts with tris(trimethylsilyl)aminoiminophosphine like its linear polyfluorinated analogues [1,2,21] to give a 76:24 mixture of two diastereomers of 2-imino-1,2-$\lambda^5\sigma^4$-oxaphosphol-4-ene (**8a**) (Scheme 7). The possible mechanism includes a nucleophilic attack of the cyclopentane carbonyl oxygen on the phosphorus atom of the phosphine to yield a $\lambda^3\sigma^3$P intermediate. The chiral phosphorus atom attacks the acyl carbonyl carbon atom inducing a new chiral centre, giving the 1,3-dipolar species **G** and **H**. **H** is obviously less favoured because of interactions of the CF_3 and $(Me_3Si)_2N$ groups. Therefore, the 1,4-Me_3Si migration prefers intermediate **G** expressed by the isomeric ratio.

Pentane-2,4-dione and tris(trimethylsilyl)aminoiminophosphine gave similarly two diastereomeric 2-imino-1,2-$\lambda^5\sigma^4$-oxaphosphol-4-ene (**8b**) (Scheme 7) in a 33:67 ratio, which however changes drastically after distillation to ca. 8:92. Possibly, warming causes 1,3-prototropy to yield the thermodynamically more stable compound.

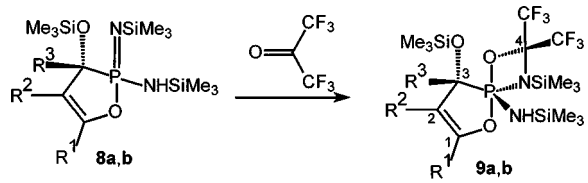
The δ_P data of **8** (27–32 ppm) are typical for tetracoordinated phosphorus. The resonance of the predominant isomer in **8b** shows a doublet of quartets ($^3J_{P-H} = 28.7$, $^3J_{P-H} = 15.5$ Hz). The ^{19}F signal of **8a** exhibits $^3J_{F-P} = 5.2$ Hz confirming the position of the CF_3 group with respect to phosphorus.



SCHEME 7

The 2-imino-1,2$\lambda^5\sigma^4$-oxaphospholens (**8**) can be stabilized by adding hexafluoracetone to give colourless, crystalline 1,3,2$\lambda^5\sigma^5$-oxazaphosphetanes (**9a,b**) (Scheme 8), converting the diastereomeric pairs of **8** to only *one* diastereomer. Compound **9a** is moisture-sensitive, unlike **9b**, which can be recrystallized from ethanol.

The molecular structure of **9a** (Fig. 2, Table 1, 2) determined by X-ray diffraction showed that both the phosphorus containing rings are axial-equatorially arranged, as in similar phosphoranes [21] with both oxygen atoms in axial position in a slightly distorted trigonal-bipyramid. The P–O distances are within the expected values of 171.8–174.6 pm for axially bonded oxygen atoms in ring systems [21,22]. In the oxaphospholene, an angle



SCHEME 8

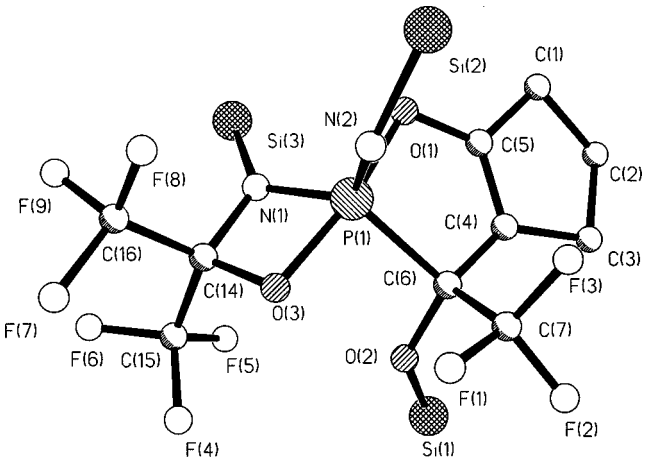


FIGURE 2 Molecular structure of compound **9a** (the methyl groups of the Me_3Si-units are omitted for clarity).

O(1)—P(1)—C(6) of 92.3° was observed and the ring atoms are co-planar with a deviation of 0.8 pm from the ideal plane. The four-membered ring is almost planar. The cyclopentane ring features a distorted "envelope" conformation with C(2), above the plane of C(1)—C(3)—C(4)—C(5) by 26.6 pm.

Only *one* set of signals was observed in the NMR spectra of phosphoranes **9**. The δ_P data are typical for compounds of this class (−15.9 ppm for **9a**, −22.2 ppm for **9b**). The magnetic non-equivalence of the geminal CF_3 groups of the oxazaphosphetane has been confirmed by ^{19}F and ^{13}C NMR data.

In conclusion, 2-polyfluoroacylcycloalkanones and their O-silylated derivates react with tris (trimethylsilyl) phosphite in a nucleophilic addition of phosphorus at the polyfluoroacyl group, followed by silatropy to afford α-polyfluoroalkyl substituted phosphonates, which hydrolyse to give the corresponding phosphonic acids. The reaction of 2-trifluoroacetylcycloalkanones with diethyl isocyanatophosphite yields phosphoranes diastereospecifically via addition of phosphorus at the trifluoroacetyl moiety and finally heterocyclisation. In the case of tris(trimethylsilyl)aminoiminophosphine, 2-imino-1,2$\lambda^5\sigma^4$-oxaphosphol-4-enes are isolated, which can be stabilized by adding hexafluoracetone. All reactions proceed without a significant influence of the ring size of the carbocycle or the chain length of the polyfluoroalkyl substitutent in the precursor 1,3-diketone.

EXPERIMENTAL

Appropriate precautions for handling moisture and oxygen-sensitive compounds were observed throughout this work. Melting and boiling points are uncorrected. MS (EI, 70eV and FAB, Xe, 8 keV, matrix—glycerin): Varian-MAT 8200 spectrometer. NMR: Bruker DPX-200 instrument at 200.1 MHz (^1H, standard TMS), 50.3 MHz (^{13}C, standard TMS), 188.3 MHz (^{19}F, standard CCl_3F), and 81.0 (^{31}P, standard 85% H_3PO_4). IR: PYE Unicam SP-300 spectrophotometer, spectra recorded in KelF oil (KBr). The single-crystal X-ray structure determinations were performed at 173(2) K on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 71.073$ pm) and a low temperature device LT2. The structures were solved by direct methods and refined by full-matrix least squares at F^2 using the SHELX-97 (Sheldrick, 1997) program system. All non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were calculated as a riding model. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre*. 2-Polyfluoroacylcycloalkanones (**1a,b** [23], **1c** [24]) were prepared by a Claisen-type condensation of cyclopentanone or cyclohexanone and the respective alkyl polyfloroacylates in the presence of sodium methylate in dried diethyl ether [23]. The O-silylated ethers **3** were prepared by a reaction of corresponding 1,3-diketones with Me_3SiCl in the presence of Et_3N according to Ref. [16].

*Reaction of 2-Trifluoroacetylcyclohexanone (**1a**) with Tris(trimethylsilyl) Phosphite*

To a solution of **1a** (1.3 g, 6.7 mmol) in dried diethyl ether (10 ml) was added dropwise, under stirring, a solution of tris(trimethylsilyl) phosphite (2.0 g, 6.7 mmol) in dried diethyl ether (10 ml). After the mixture had been stirred for 1 h, the solvent was removed in vacuo, and the product was allowed to crystallize at ambient temperature. The crystals were washed with cold hexane (2 × 2 ml). The product was obtained as 1.5 g (46%) of colorless crystals (mp 60–62°C). ^1H NMR (C_6D_6) (**2a**): $\delta = 0.09$ [s, 9H, $3CH_3$], 0.20 [s, 9H, $3CH_3$], 0.32 [s, 9H, $3CH_3$], 1.25–1.44 (m, 4H, $2CH_2$), 1.8 (br s, 2H, CH_2), 2.29, 2.64 (AB-system, 2H, CH_2, $J_{Ha-Hb} = 16.2$ Hz), 7.29 (d, 1H, $^3J_{H-P} = 7.3$ Hz, the signal disappears upon adding CD_3COOD). ^{13}C NMR (C_6D_6) (**2a**): $\delta = 0.9$ [s, CH_3], 1.0 [d, CH_3, $^3J_{C-P} = 0.9$ Hz], 1.3 [d, CH_3, $^3J_{C-P} = 0.9$ Hz],

*Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 164035 (**6b**) and CCDC 164036 (**9a**). Copies of the data can be obtained on application to the director, CCDC; 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-23 336-033); e-mail; deposit@ccdc.cam.ac.uk.

22.6, 22.9, 26.0 [three s, C^3, C^4, C^5], 31.4 [s, C^6], 79.2 [dq, C^7, $^1J_{C-P} = 175.1$, $^2J_{C-F} = 28.6$ Hz], 109.5 [s, C^2], 125.5 [qd, CF_3, $^1J_{C-F} = 286.7$, $^2J_{C-P} = 7.5$ Hz], 151.0 [d, C^1, $^3J_{C-P} = 9.8$ Hz]. ^{19}F NMR (C_6D_6) (**2a**): $\delta = -72.78$ [d, $^3J_{F-P} = 5.2$ Hz]. ^{31}P NMR (C_6D_6) (**2a**): $\delta = -1.4$ br s. ^{31}P{^{1}H} NMR (C_6D_6) (**2a**): $\delta = -1.40$ [q, $^3J_{P-F} = 5.1$ Hz]. ^{1}H NMR (C_6D_6) (**2b**): $\delta = 0.05$ [s, 9H, $3CH_3$], 0.18 [s, 9H, $3CH_3$], 0.22 [s, 9H, $3CH_3$], 1.15–1.39 [m, 8H, $4CH_2$]. ^{19}F NMR (C_6D_6) (**2b**): $\delta = -72.85$ [d, $^3J_{F-P} = 5.2$ Hz]. ^{31}P NMR (C_6D_6) (**2b**): $\delta = 1.2$ br s. ^{31}P{^{1}H} NMR (C_6D_6) (**2b**): $\delta = 1.23$ unresolv q. Ratio [**2a**]:[**2b**] = 94:6 (^{1}H NMR), 93:7 (^{19}F NMR), 95:5 (^{31}P NMR), 94:6 (^{31}P{^{1}H} NMR). MS (EI, 19°C); *m/z* (%): 492 (4) [M^+], 477 (8) [$M - Me]^+$, 226 (100) [$HPO(OSiMe_3)_2]^+$, 211 (44) [$HPO(OSiMe_3)_2$–$Me]^+$, 73 (62) [$SiMe_3]^+$, and other fragments. HRMS for $C_{17}H_{36}F_3O_5PSi_3$; Calcd.: 492.1560. Found: 492.1573.

*[2,2,2-Trifluoro-1-(1-trimethylsiloxycyclohex-1-ene-2-yl)-1-trimethylsiloxyethyl]bis(trimethylsilyl)phosphonate (**4a**)*

To a solution of **3a** (3.0 g, 11 mmol) in dried diethyl ether (20 ml) was added dropwise, under stirring, a solution of tris(trimethylsilyl) phosphite (3.4 g, 11 mmol) in dried diethyl ether (10 ml) within 0.5 h at room temperature. After the mixture had been stirred for 1 h, the volatile materials were removed in vacuo, and the residue was distilled to give 4.5 g (73%) of **4a** as a viscous colorless oil (bp 54–64°C (0.5 Torr)). ^{1}H NMR (C_6D_6): $\delta = 0.17$ [s, 9H, $3CH_3$], 0.23 [s, 9H, $3CH_3$], 0.24 [d, 18H, $6CH_3$, $^4J_{H-P} = 2.0$ Hz], 1.26–1.53 [m, 4H, $2CH_2$], 1.89–2.57 [m, 4H, $2CH_2$]. ^{13}C NMR (C_6D_6): $\delta = 1.1$ [d, CH_3, $^3J_{C-P} = 1.5$ Hz], 1.2 [d, CH_3, $^3J_{C-P} = 1.5$ Hz], 1.9 [m, CH_3], 2.0 [s, CH_3], 23.2, 23.5 [two s, $2CH_2$], 26.6 [m, C^3], 32.8 [d, C^4, $^4J_{C-P} = 2.3$ Hz], 81.2 [dq, C^5, $^1J_{C-P} = 181.2$, $^2J_{C-F} = 29.0$ Hz], 107.9 [d, C^2, $^2J_{C-P} = 3.8$ Hz], 125.5 [qd, CF_3, $^1J_{C-F} = 288.8$, $^2J_{C-P} = 7.4$ Hz], 150.1 [d, C^1, $^3J_{C-P} = 8.7$ Hz]. ^{19}F NMR (C_6D_6): $\delta = -66.43$ [d, $^3J_{F-P} = 8.6$ Hz]. ^{31}P NMR (C_6D_6): $\delta = -2.2$ m. ^{31}P{^{1}H} NMR (C_6D_6): $\delta = -2.22$ [q, $^3J_{P-F} = 8.6$ Hz]. MS (EI, 66°C); *m/z* (%): 564 (2) [M^+], 549 (4) [$M - Me]^+$, 339 (34) [$M - PO(OSiMe_3)_2]^+$, 225 (5) [$PO(OSiMe_3)_2]^+$, 197 (11) [$M - PO(OSiMe_3)_2 - CF_3 - SiMe_3]^+$, 73 (50) [$SiMe_3]^+$, and other fragments. HRMS for $C_{20}H_{44}F_3O_5PSi_4$; Calcd.: 564.1956. Found: 564.1950.

*[2,2,3,3,4,4,4-Heptafluoro-1-(1-trimethylsiloxybutyl-1-trimethylsiloxycyclopent-1-ene-2-yl)]bis(trimethylsilyl)phosphonate (**4b**)*

To a solution of **3b** (2.4 g, 6.8 mmol) in dried diethyl ether (15 ml) was added dropwise, under stirring, a solution of tris(trimethylsilyl) phosphite (2.0 g, 6.8 mmol) in dried diethyl ether (5 ml) within 0.5 h at room temperature. After the mixture had been stirred for 1 h, the volatile materials were removed in vacuo, and the residue was distilled through a Vigreaux column to give 2.4 g (75%) of **4b** as a viscous colorless oil (bp 44–46°C (0.5 Torr)). ^{1}H NMR (C_6D_6): $\delta = 0.14$ [s, 9H, $3CH_3$], 0.20 [d, 18H, $6CH_3$, $^4J_{H-P} = 3.4$ Hz], 0.30 [s, 9H, $3CH_3$], 1.55–2.70 [m, 6H, $3CH_2$]. ^{13}C NMR (C_6D_6): $\delta = 1.1$ [s, CH_3], 1.3 [m, CH_3], 2.6 [br s, CH_3], 2.0 [s, CH_3], 19.5 [s, CH_2], 32.3 [s, C^3], 36.4 [d, C^4, $^4J_{C-P} = 2.6$ Hz], 80.9 [dt, C^5, $^1J_{C-P} = 164.2$, $^2J_{C-F} = 27.8$ Hz], 108.1 [br s, C^2], 104.9–123.4 [ms, C_3F_7], 151.1 [d, C^1, $^3J_{C-P} = 8.2$ Hz]. ^{19}F NMR (C_6D_6): $\delta = -124.8$, -123.9 [AB-system d, 2F, CF_2, $J_{Fa-Fb} = 282.5$, $^3J_{F-P} = 8.6$ Hz], -110.44 [m, 2F, CF_2], -82.32 [t, 3F, CF_3, $^4J_{F-F} = 11.2$ Hz]. ^{31}P NMR (C_6D_6): $\delta = -1.2$ br s (according to ^{1}H and ^{31}P NMR data ca. 15% impurity of tris(trimethylsilyl) phosphite). MS (EI, 56°C); *m/z* (%): 650 (0.2) [M^+], 635 (1) [$M - Me]^+$, 425 (4) [$M - PO(OSiMe_3)_2]^+$, 73 (64) [$SiMe_3]^+$, and other fragments.

*Morpholinium-3-trifluoromethyl-2,4,5,6-tetrahydro-2-oxobenzo-[d]-1,2λ^5-oxaphosphol-2-ate (**5**)*

To a solution of **4a** (3.0 g, 5 mmol) in THF (20 ml) was added water (3.0 ml). After the mixture had been stirred for 1 h at room temperature, the volatile materials were removed in vacuo, the residue was heated for 15 min (temperature of oil bath 200°C) and dissolved in $CHCl_3$ (5 ml). Morpholine (2 g, 23 mmol) was added, and after stirring of the mixture for 0.5 h at room temperature, the volatile materials were removed in vacuo. The solid residue was precipitated with hexane from toluene and was then recrystallized from petrol ether $CHCl_3$ (1:2) to afford 0.5 g (29%) of **5** as yellowish crystals, mp 179–182°C. ^{1}H NMR (DMSO-d_6): $\delta = 1.56$–1.69 [m, 2H, CH_2], 2.09–2.28 [m, 2H, CH_2], 2.50–2.68 [m, 2H, CH_2], 2.95–3.00 [m, 4H, $2CH_2$ (morpholinium)], 3.71–3.75 [m, 4H, $2CH_2$ (morpholinium)], 5.43 [t, 1H, =CH, $^3J_{H-H} = 4.6$ Hz], 9.5 [br s, 2H, NH_2]. ^{13}C NMR (DMSO-d_6): $\delta = 22.6$, 23.6 [two s, $2CH_2$], 25.1 [d, C^3, $^3J_{C-P} = 13.3$ Hz], 43.5, 64.1 [two s, CH_2-morpholinium], 108.0 [dq, C^2, $^2J_{C-P} = 10.1$, $^3J_{C-F} = 0.9$ Hz], 119.6 [dq, C^5, $^1J_{C-P} = 158.1$, $^2J_{C-F} = 33.1$ Hz], 125.0 [qd, CF_3, $^1J_{C-F} = 269.8$, $^2J_{C-P} = 18.8$ Hz], 147.0 [d, C^4, $^3J_{C-P} = 9.7$ Hz], 147.0 [dq, C^1, $^2J_{C-P} = 13.3$, $^4J_{C-F} = 5.5$ Hz]. ^{19}F NMR ($CDCl_3$): $\delta = -57.23$ [d, $^3J_{F-P} = 8.9$ Hz]. ^{31}P NMR ($CDCl_3$): $\delta = 23.19$ [q, $^3J_{P-F} = 8.9$ Hz]. MS (FAB, 26°C); positive *m/z* (%): 328 (15) [$C_8H_7F_3O_3P + H + C_4H_{10}NO]^+$, 88 (100) [$C_4H_{10}NO]^+$, and other fragments; negative *m/z* (%): 479 (8) [$2C_8H_7F_3O_3P + H]^-$, 257 (15)

$[C_8H_7F_3O_3P + H_2O]^-$, 239 (100) $[C_8H_7F_3O_3P]^-$, 220 (14) $[C_8H_7F_3O_3P{-}F]^-$, and other fragments. Anal. calcd. for $C_{12}H_{17}F_3NO_4P$ (327.24): C, 44.04; H, 5.24; N, 4.28. Found: C, 43.95; H, 5.56; N, 4.27.

*Potassium-[1-(cyclohexane-1-on-2-yl)-2,2,2-trifluoro-1-hydroxyethyl]phosphonate (**6a**)*

To a solution of a mixture of **2a** and **2b** (1.5 g) in THF (10 ml) was added water (0.5 ml). After stirring the mixture for 0.5 h at room temperature, the volatile materials were removed in vacuo, and the residue was purified by column chromatography (eluent: ethylacetate). There was obtained 0.4 g of a colorless oil. To a solution of this oil in propan-2-ol (2 ml) was added a solution of KOH (0.08 g, 1.5 mmol) in propan-2-ol (3 ml + two drops of water). The mixture was cooled to −30°C, and the precipitate was filtered off, dried and recrystallized from *i*-PrOH:H_2O (3:1) to afford 0.25 g (27%) of **6a** as colorless crystals (mp 240–245°C). ^{1}H NMR (DMSO-d_6) (Form **C**): $\delta = 1.19$–1.93 (m, 8H, $4CH_2$), 2.2 [br s, 1H, OH], 4.44–4.63 [m, 1H, CH], 6.1 [br s, 1H, OH]. ^{19}F NMR (DMSO-d_6): $\delta = -73.12$ [d, $^3J_{F-P} = 5.2$ Hz] (Form [**C**), −72.62 m (Form **D**). ^{31}P NMR (DMSO-d_6): $\delta = 17.55$ m (Form **C**), 22.12 (Form **D**). Ratio [**C**]:[**D**] = 72:28 (^{19}F, ^{31}P NMR). IR: ν/cm^{-1} = 1695 [C=O], 2880, 2960 [C–H], 3000–3640 [OH]. MS (FAB, 28°C); positive *m/z* (%): 391 (26) $[C_8H_{11}F_3PO_5 + 3K - H]^+$, 353 (100) $[C_8H_{11}F_3PO_5 + 2K]^+$, and other fragments; negative *m/x* (%): 275 (95) $[C_8H_{11}F_3PO_5]^-$, 193 (26) $[C_8H_8F_3O_2]^-$, 177 (100) $[C_8H_{11}F_3PO_5{-}C_6H_{10}O]^-$, 97 (6) $[C_6H_9O]^-$, 81 (26) $[H_2PO_3]^-$, 79 (31) $[PO_3]^-$, and other fragments.

*Potassium-[1-(cyclopentane-1-on-2-yl)-2,2,3,3,4,4,4-heptafluoro-1-hydroxybutyl]phosphonate (**6b**)*

To a solution of **4b** (1.2 g, 1.8 mmol) in THF (3 ml) was added water (0.5 ml). After stirring of the mixture for 0.5 h at room temperature, the volatile materials were removed in vacuo, and to a solution of the residue in ethanol (2 ml) was added a solution of KOH (0.08 g, 1.5 mmol) in ethanol (3 ml). The mixture was cooled to −30°C, and the precipitate was filtered off, dried, and recrystallized from *i*-PrOH:H_2O (2:1) to afford 0.3 g (41%) of **6b** as colorless crystals (mp 224–225°C (with decomposition)). ^{1}H NMR (DMSO-d_6) (Form **C**): $\delta = 1.35$–2.30 (m, 6H, $3CH_2$), 3.7 [br s, 1H, OH], 4.5 [br s, 1H, CH], 5.3 [br s, 1H, OH]. ^{19}F NMR (DMSO-d_6): $\delta = -122.75$ [s, 2F, CF_2], −112.43 [m, 2F, CF_2], −81.22 [t, 3F, CF_3, $^4J_{F-F} = 10.4$ Hz] (Form **C**); −123.93 [m, 2F, CF_2], −115.46 [m, 2F, CF_2], −81.33 [t, 3F, CF_3, $^4J_{F-F} = 10.3$ Hz] (Form **D**). ^{31}P NMR (DMSO-d_6): $\delta = 10.16$ m (Form **C**), 27.13 m (Form **D**). Ratio [**C**]:[**D**] = 83:17 (^{19}F, ^{31}P NMR). IR: ν/cm^{-1} = 1725 [C=O], 2870, 2940 [C–H], 3400, 3580 [OH]. MS (FAB, 29–30°C); positive *m/z* (%): 438 (92) $[C_9H_9F_7O_5P - H + 2K]^+$, and other fragments; negative *m/z* (%): 361 (80) $[C_9H_9F_7O_5P]^-$, 279 (40) $[C_9H_6F_7O_2]^-$, 277 (100) $[C_9H_9F_7O_5P - C_5H_8O]^-$, 81 (13) $[H_2PO_3]^-$, 79 (42) $[PO_3]^-$, and other fragments.

*Morpholinium-[1-(cyclopentane-1-on-2-yl)-2,2,3,3,4,4,4-heptafluoro-1-hydroxybutyl]phosphonate (**6c**)*

To a solution of **4b** (1.2 g, 1.8 mmol) in THF (3 ml) was added water (1.0 ml). After stirring of the mixture for 1 h at room temperature, the volatile materials were removed in vacuo, and to a solution of the residue in ethanol (2 ml) was added morpholine (0.32 g, 3.7 mmol). The mixture was cooled to −30°C, and the precipitate was filtered off, washed with boiling $CHCl_3$, dried, and recrystallized from EtOH:H_2O (10:1), and then from H_2O to afford 0.8 g (46%) of **6c** as colorless crystals (mp 214–216°C (with decomposition)). ^{1}H NMR (DMSO-d_6) (Form **C**): $\delta = 1.40$–2.40 [m, 6H, $3CH_2$], 3.0 [br s, 4H, $2CH_2$ (morpholinium)], 3.6 [br s, 1H, OH], 3.7 [br s, 4H, $2CH_2$ (morpholinium)], 4.7 [br s, 1H, CH], 5.5 [br s, 1H, OH]. ^{19}F NMR (DMSO-d_6): $\delta = -123.61$, −122.51 [AB-system, 2F, CF_2, $J_{Fa-Fb} = 283.7$ Hz], −113.17 [s, 2F, CF_2], −81.33 [t, 3F, CF_3, $^4J_{F-F} = 11.2$ Hz] (Form **C**); −123.94 [m, 2F, CF_2], −115.46 [m, 2F, CF_2], −81.11 [t, 3F, CF_3, $^4J_{F-F} = 10.3$ Hz] (Form **D**). ^{31}P NMR (DMSO-d_6): $\delta = 10.40$ m (Form **C**), 27.46 m (Form **D**). Ratio [**C**]:[**D**] = 52:48 (^{19}F, ^{31}P NMR). IR: ν/cm^{-1} = 1730 [C=O], 2870, 2980 [C–H], 3180–3600 [OH]. MS (FAB, 25–27°C); positive *m/z* (%): 450 (10) $[C_9H_9F_7O_5P + H + C_4H_{10}NO]^+$, 88 (100) $[C_4H_{10}NO]^+$, and other fragments; negative *m/z* (%): 361 (100) $[C_9H_9F_7O_5P]^-$, 279 (28) $[C_9H_6F_7O_2]^-$, 277 (55) $[C_9H_9F_7O_5P - C_5H_8O]^-$, 81 (8) $[H_2PO_3]^-$, 79 (24) $[PO_3]^-$, and other fragments. Anal. calcd. for $C_{13}H_{19}F_7NO_6P \cdot H_2O$ (467.27): C, 33.42; H, 4.53; N, 3.00. Found: C, 33.23; H, 4.32; N, 2.87.

*1,1-Diethoxy-5-trifluoromethyl-6,7-tetramethylene-4,8-dioxa-2-aza-1λ^{5}σ^5-phosphabicyclo-[3.3.0]-oct-6-ene-3-one (**7a**)*

To a solution of **1a** (2.0 g, 10 mmol) in dried diethyl ether (10 ml) was added dropwise, under stirring, a solution of diethyl isocyanatophosphite (1.7 g, 10 mmol) in dried diethyl ether (10 ml) within 0.5 h at room temperature. After stirring the mixture for 0.5 h, the volatile materials were removed

in vacuo, and the residue was allowed to crytallize at −30°C. The solid was washed with boiling hexane (3 ml) and recrystallized from hexanetoluene (1:1) to afford 1.6 g (45%) of **7a** as colorless crystals (mp 129–130°C). ^{1}H NMR (C_6D_6): $\delta = 0.96$ [td, 3H, C^9H_3, $^3J_{H-H} = 7.0$, $^4J_{H-P} = 1.4$ Hz], 1.12 [t, 3H, $C^{10}H_3$, $^3J_{H-H} = 6.8$ Hz], 1.16–1.34 [m, 4H, $2CH_2$], 1.7 [br s, 2H, CH_2], 1.98–2.20 [m, 2H, CH_2], 3.63–3.96 [m, 4H, C^7H_2, C^8H_2], 8.4 [br s, 1H, NH]. ^{13}C NMR (C_6D_6): $\delta = 15.7$ [d, C^9, $^3J_{C-P} = 8.3$ Hz], 16.3 [d, C^{10}, $^3J_{C-P} = 9.6$ Hz], 21.8, 22.4 [two s, $2CH_2$], 21.5 [d, $C^{3(4)}$, $^3J_{C-P} = 8.8$ Hz], 24.3 [d, $C^{4(3)}$, $^3J_{C-P} = 11.4$ Hz], 61.6 [d, C^7, $^2J_{C-P} = 9.6$ Hz], 67.3 [d, C^8, $^2J_{C-P} = 15.8$ Hz], 87.5 [dq, C^6, $^1J_{C-P} = 124.1$, $^2J_{C-F} = 30.7$ Hz], 110.8 [d, C^5, $^2J_{C-P} = 14.0$ Hz], 125.5 [q, CF_3, $^1J_{C-F} = 282.2$ Hz], 154.6 [d, C^2, $^2J_{C-P} = 3.1$ Hz], 157.4 [d, C^1, $^2J_{C-P} = 30.3$ Hz]. ^{19}F NMR (C_6D_6): $\delta = -70.93$ s. ^{31}P NMR (C_6D_6): $\delta = -49.03$ s. MS (EI, 86°C); *m/z* (%): 357 (38) $[M^+]$, 312 (64) $[M - EtO]^+$, 284 (40) $[M - Et - CO_2]^+$, 266 (72) $[M - EtO - EtOH]^+$, 238 (100) $[M - Et - CO_2 - EtOH]^+$, and other fragments. Anal. calcd. for $C_{13}H_{19}F_3NO_5P$ (357.26): C, 43.70; H, 5.36; F, 16.0; P, 8.67. Found: C, 43.53; H, 5.32; F, 15.9; P, 8.47.

*1,1-Diethoxy-5-trifluoromethyl-6,7-trimethylene-4,8-dioxa-2-aza-1λ^{5}σ^5-phosphabicyclo-[3.3.0]-oct-6-ene-3-one (**7b**)*

To a solution of **1b** (2.0 g, 11 mmol) in dried diethyl ether (10 ml) was added dropwise, under stirring, a solution of diethyl isocyanatophosphite (1.8 g, 11 mmol) in dried diethyl ether (10 ml) within 0.5 h at room temperature. After stirring the mixture for 0.5 h, the volatile materials were removed in vacuo, and the product was allowed to crystalize at −30°C. After recrystallization from hexanetoluene (3:2) there was obtained 1.9 g (50%) of **7b** as colorless crystals (mp 123–124°C). ^{1}H NMR (C_6D_6): $\delta = 0.95$ [td, 3H, C^9H_3, $^3J_{H-H} = 7.1$, $^4J_{H-P} = 1.2$ Hz], 1.13 [td, 3H, $C^{10}H_3$, $^3J_{H-H} = 7.0$, $^4J_{H-P} = 1.3$ Hz], 3.67–3.93 [m, 4H, C^7H_2, C^8H_2], 1.39–1.54 [m, 2H, CH_2], 1.87–1.94 [m, 2H, CH_2], 2.25–2.32 [m, 2H, CH_2], 8.5 [br s, 1H, NH]. ^{13}C NMR (C_6D_6): $\delta = 15.7$ [d, C^9, $^3J_{C-P} = 7.9$ Hz], 16.3 [d, C^{10}, $^3J_{C-P} = 9.6$ Hz], 21.3 [s, CH_2], 25.8 [d, $C^{3(4)}$, $^3J_{C-P} = 6.1$ Hz], 27.9 [d, $C^{4(3)}$, $^3J_{C-P} = 7.0$ Hz], 61.8 [d, C^7, $^2J_{C-P} = 9.6$], 67.6 [d, C^8, $^2J_{C-P} = 16.7$ Hz], 88.3 [dq, C^6, $^1J_{C-P} = 129.6$, $^2J_{C-F} = 31.3$ Hz], 114.6 [d, C^5, $^2J_{C-P} = 14.0$ Hz], 125.3 [qd, CF_3, $^1J_{C-F} = 280.9$, $^2J_{C-P} = 1.8$ Hz], 157.4 [d, C^1, $^2J_{C-P} = 30.7$ Hz], 161.2 [d, C^2, $^2J_{C-P} = 3.5$ Hz]. ^{19}F NMR (C_6D_6): $\delta = -71.90$ s. ^{31}P NMR (C_6D_6): $\delta = -35.76$ s. MS (EI, 109°C); *m/z* (%): 343 (40) $[M^+]$, 290 (90) $[M - EtO]^+$, 270 (65) $[M - Et - CO_2]^+$, 224 (100) $[M - Et - CO_2 - EtOH]^+$, 29 (74) $[Et]^+$, and other fragments. HRMS for $C_{12}H_{17}F_3NO_5P$; Calcd.: 343.0797. Found: 343.0787.

*3-Trifluoromethyl-4,5-trimethylene-2-trimethylsilylamino-2-trimethylsilylimino-3-trimethylsiloxy-1,2λ^{5}σ^4-oxaphosphol-4-ene (**8a**)*

To a solution of **1b** (1.5 g, 8.2 mmol) in dried diethyl ether (20 ml) was added dropwise, under stirring, a solution of tris(trimethylsilyl) aminoiminophosphine (2.3 g, 8.2 mmol) in dried diethyl ether (10 ml) within 0.5 h at −50°C. After stirring the mixture for 0.5 h at −50°C, the volatile materials were removed in vacuo to give 2.6 g (69%) of **8a** as a yellowish oil. ^{19}F NMR (Et_2O): $\delta = -73.28$ [d, diastereomer **X**, $^3J_{F-P} = 5.2$ Hz], −72.77 [d, diastereomer **Y**, $^3J_{F-P} = 5.2$ Hz]. ^{31}P NMR (Et_2O): $\delta = 26.57$ [s, diastereomer **X**], 27.53 [s, diastereomer **Y**]. Ratio [**X**]:[**Y**] = 76:24 (^{19}F NMR), 77:23 (^{31}P NMR). MS (EI, 54°C); *m/z* (%): 458 (50) $[M^+]$, 443 (40) $[M - Me]^+$, 297 (30) $[M - Me_3SiNH - Me_3Si]^+$, 73 (100) $[Me_3Si]^+$, and other fragments.

*3,5-Dimethyl-2-trimethylsilylamino-2-trimethylsilylimino-3-trimethylsiloxy-1,2λ^{5}σ^4-oxaphosphol-4-ene (**8b**)*

To a solution of pentane-2,4-dione (1.1 g, 10 mmol) in dried diethyl ether (5 ml) was added dropwise, under stirring, a solution of tris(trimethylsilyl) aminoiminophosphine (3.0 g, 10 mmol) in dried diethyl ether (5 ml) within 15 min at −50°C. After stirring of the mixture for 0.5 h at −50°C, the volatile materials were removed in vacuo, and the residue was distilled to give 2.1 g (56%) of **8b** as a colorless oil (bp 71–74°C (0.5 Torr)). ^{1}H NMR (C_6D_6) (diastereomer **X**): $\delta = 0.03$ [s, 9H, $3CH_3$], 0.26 [s, 18H, $6CH_3$], 1.50 [d, 3H, CH_3, $^3J_{H-P} = 16.0$ Hz], 1.62 [s, 3H, CH_3], 4.66 [d, 1H, =CH, $^3J_{H-P} = 26.4$ Hz]. ^{31}P NMR (C_6D_6) (diastereomer **X**): $\delta = 29.8$ m. ^{1}H NMR (C_6D_6) (diastereomer **Y**): $\delta = 0.10$ [s, 9H, $3CH_3$], 0.29 [s, 18H, $6CH_3$], 1.53 [d, 3H, CH_3, $^3J_{H-P} = 16.0$ Hz], 1.62 [s, 3H, CH_3], 2.9 [br s, 1H, NH], 4.76 [d, 1H, =CH, $^3J_{H-P} = 27.9$ Hz]. ^{13}C NMR (C_6D_6) (diastereomer **Y**): 1.3 [d, CH_3, $^3J_{C-P} = 1.8$ Hz], 2.3, 3.8 [two s, $2CH_3$], 17.1 [d, CH_3, $^2J_{C-P} = 4.4$ Hz], 23.9 [d, CH_3, $^3J_{C-P} = 5.3$ Hz], 74.8 [d, C^3, $^1J_{C-P} = 130.7$ Hz], 109.1 [d, C^2, $^2J_{C-P} = 16.7$ Hz], 154.6 [d, C^1, $^2J_{C-P} = 7.9$ Hz]. ^{31}P NMR (C_6D_6) (diastereomer **Y**): $\delta = 32.10$ [dq, $^3J_{P-H} = 28.7$, $^3J_{P-H} = 15.5$ Hz]. Ratio [**X**]:[**Y**] = 8:92 (^{1}H, ^{31}P NMR). MS (EI, 200°C); *m/z* (%): 378 (23) $[M^+]$, 363 (10) $[M - Me]^+$, 73 (24) $[Me_3Si]^+$, and other fragments. HRMS for $C_{14}H_{35}N_2O_2PSi_3$; Calcd.: 378.1744. Found: 378.1743.

*2,2,8-Tris(trifluoromethyl)-6,7-trimethylene-3-trimethylsilyl-4-trimethylsilylamino-8-trimethylsiloxy-1,5,3λ^{5}σ^5-dioxaza-4-phosphaspiro-[3.4]-oct-6-ene (***9a***)*

To a solution of **8a** (3.7 g, 8 mmol) in dried diethyl ether (20 ml) contained in a thick-walled glass ampoule equipped with a teflon tap was condensed hexafluoroacetone (1.5 g, 9 mmol), at −196°C in vacuo and the solution was warmed to ambient temperature. The volatile materials were removed in vacuo, and the residue was dissolved in dried hexane (5 ml). The solvent was pumped off, and the solid residue was recrystallized from hexane to give 3.0 g (60%) of **9a** as colorless crystals (mp 89–91°C). ^{1}H NMR (C_6D_6): δ = −0.04 [s, 9H, $3CH_3$], 0.20 [s, 9H, $3CH_3$], 0.24 [s, 9H, $3CH_3$], 1.55–1.70 [m, 2H, CH_2], 2.24–2.45 [m, 2H, CH_2], 2.04 [t, 2H, CH_2, $^3J_{H-H}$ = 16 Hz]. ^{13}C NMR (C_6D_6): δ = 1.1 [d, CH_3, $^3J_{C-P}$ = 3.1 Hz], 1.3, 2.4 [two s, $2CH_3$], 21.9 [s, CH_2], 28.0 [d, CH_2, $^3J_{C-P}$ = 12.7 Hz], 29.3 [q, CH_2, $^4J_{C-F}$ = 2.6 Hz], 82.9 [dq, C^3, $^1J_{C-P}$ = 174.8, $^2J_{C-F}$ = 32.3 Hz], 110.9 [d, C^2, $^2J_{C-P}$ = 18.9 Hz], 122.2 [qd, CF_3, $^1J_{C-F}$ = 289.0, $^3J_{C-P}$ = 9.6 Hz], 123.0 [qd, CF_3, $^1J_{C-F}$ = 287.1, $^3J_{C-P}$ = 2.2 Hz], 125.1 [qd, CF_3, $^1J_{C-F}$ = 288.7, $^2J_{C-P}$ = 13.4 Hz], 162.2 [d, C^1, $^2J_{C-P}$ = 4.8 Hz]. ^{19}F NMR (C_6D_6): δ = −78.72 [q, 3F, CF_3, $^4J_{F-F}$ = 8.6 Hz], −71.80 [q, 3F, CF_3, $^4J_{F-F}$ = 8.6 Hz], −69.18 [d, 3F, CF_3, $^3J_{F-P}$ = 6.9 Hz]. ^{31}P NMR (C_6D_6): δ = −15.9 br s. MS (EI, 53°C); *m/z* (%): 624 (40) [M^+], 555 (4) [$M - CF_3$]$^+$, 535 (4) [$M - Me_3SiO$]$^+$, 461 (28) [$M - (Me_3Si)_2O - H$]$^+$, 208 (100) [$M - Me_3SiNH - Me_3SiO - (CF_3)_2CO - Me_3Si$]$^+$, 73 (90) [$Me_3Si$]$^+$, and other fragments. HRMS for $C_{19}H_{34}F_9N_2O_3PSi_3$; (0.7 g, 4 mmol). Calcd.: 624.1471. Found: 624.1485.

*2,2-Bis(trifluoromethyl)-6,8-dimethyl-3-trimethylsilyl-4-trimethylsilylamino-8-trimethylsiloxy-1,5,3λ^{5}σ^5-dioxaza-4-phosphaspiro-[3.4]-oct-6-ene (***9b***)*

To a solution of **8b** (1.0 g, 2.5 mmol) in dried diethyl ether (5 ml) contained in a thick-walled glass ampoule equipped with a teflon tap was condensed hexafluoroacetone (0.7 g, 4 mmol) at −196°C in vacuo, and the solution was warmed to ambient temperature. The volatile materials were removed in vacuo, and the solid residue was recrytsallized twice from hexane at −30°C to give 0.9 g (66%) of **9b** as colorless crystals (mp 73–75°C). ^{1}H NMR (C_6D_6): δ = −0.01 [s, 9H, $3CH_3$], 0.17 [s, 9H, $3CH_3$], 0.26 [s, 9H, $3CH_3$], 1.5 [br s, 3H, CH_3], 1.52 [d, 3H, CH_3, $^3J_{H-P}$ = 19.6 Hz], 2.16 [d, 1H, NH, $^2J_{H-P}$ = 5.4 Hz], 4.74 [d.q, 1H, =CH, $^3J_{H-P}$ = 43.0, $^4J_{H-H}$ = 1.1 Hz]. ^{13}C NMR (C_6D_6): δ = 1.2 [d, CH_3, $^3J_{C-P}$ = 4.4 Hz], 1.2, 2.5 [two s, $2CH_3$], 17.4 [d, CH_3, $^2J_{C-P}$ = 3.5 Hz], 23.6 [d, CH_3, $^3J_{C-P}$ = 5.3 Hz], 79.6 [d, C^3, $^1J_{C-P}$ = 170.1 Hz], 83.7 [sept d, C^4, $^2J_{C-F}$ = 33.8, $^2J_{C-P}$ = 8.5 Hz], 107.9 [d, C^2, $^2J_{C-P}$ = 21.0 Hz], 122.5 [qd, CF_3, $^1J_{C-F}$ = 290.0, $^3J_{C-P}$ = 9.6 Hz], 123.4 [q, CF_3, $^1J_{C-F}$ = 290.0 Hz], 152.7 [d, C^1, $^2J_{C-P}$ = 9.6 Hz]. ^{19}F NMR (C_6D_6): δ = −79.42 [q, 3F, CF_3, $^4J_{F-F}$ = 8.6 Hz], −71.47 [q, 3F, CF_3, $^4J_{F-F}$ = 8.6 Hz]. ^{31}P NMR (C_6D_6): δ = −22.2 [md, $^2J_{P-H}$ = 5.3 Hz]. ^{31}P{^{1}H} NMR (C_6D_6): δ = −22.24 s. Anal. calcd. for $C_{17}H_{35}F_6N_2O_3PSi_3$ (544.69): C, 37.49; H, 6.48. Found: C, 37.61; H, 6.48.

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